

# PATENT SPECIFICATION

NO DRAWINGS

828,231



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International Classification:—C07c, D06m.

## COMPLETE SPECIFICATION

### Improvements relating to Insecticidal Compounds and their use

We, J. R. GEIGY A.—G., a body corporate organised according to the laws of Switzerland, of 215 Schwarzwaldallee, Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

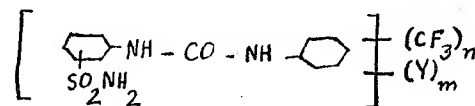
The present invention concerns insecticidal agents, processes for the production thereof and their use for the protection of keratine material against destruction caused by injurious insects. The invention also concerns, as industrial product, the material protected by these agents from destruction caused by injurious insects.

Various processes concerning the production of sulphonated insecticidal agents are already known. However, compounds with sulphonic acid groups only draw completely onto keratine material, for example, wool, from a relatively strongly acid bath. Insecticidal agents are often applied in the dyebath when dyeing the wool. When dyestuffs needing only a slight amount of acid or having slight migratory power are used, such as for example complex heavy metal compounds of monoazo dyestuffs having no acid dissociating groups, the presence of acid in the dyebath has an adverse effect on the evenness of the wool dyeing. There is, therefore, a need for insecticidal agents which draw onto wool from a neutral to weakly acid dyebath and can, therefore, be applied with complex heavy metal compounds of unsulphonated azo dyestuffs. Thus, protective agents against injurious insects which have sufficient drawing power from a neutral bath are a valuable contribution to the art.

In this connection, the treatment of keratine material with insecticidal agents which have no sulphonic acid groups and are insoluble in water has already been suggested. This was done by using aqueous emulsions of such agents in the preparation of the dyebaths. However, it is difficult to make such emul-

sions durable and often undesirable precipitates occur in the dyebath.

It has now been found that water soluble compounds having no sulphonic acid groups, which compounds have good activity against insects that are injurious to keratine fibres, are obtained if an isocyanate of the aromatic series is reacted with an aromatic amine, the components being so chosen that an  $H_2N - SO_2 -$  group is introduced with the aromatic amine and at least two substituents selected from aromatically bound halogen atoms or trifluoromethyl groups are present in the reaction product, which corresponds with the formula:



wherein Y represents a halogen atom

n represents an integer from 0 — 2 and

m represents an integer from 0 — 5

and wherein  $n + m$  are at least 2.

For technical and economical reasons, chiefly chlorine is meant by halogen atoms, however, the corresponding derivatives substituted by bromine, fluorine and iodine can also be used.

The insecticidal compounds produced according to the present invention are new. Their production by reacting isocyanates of the aromatic series with the aromatic amino compounds occurs under conditions which are usual for such reactions which are known per se.

4 - Chlorophenyl isocyanate, 3,4 - dichlorophenyl isocyanate, 3,4,5 - trichlorophenyl isocyanate, 3 - trifluoro - methylphenyl isocyanate, 3 - trifluoromethyl - 4 - chlorophenyl isocyanate and 3 - chloro - 4 - trifluoromethylphenyl isocyanate can be used as aromatic isocyanates.

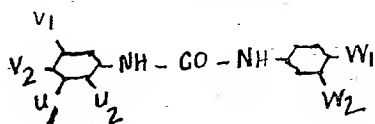
Examples of aromatic amines which can be

[Price 3s. 6d.]

used are 2- or 3- or 4-aminobenzene sulphon-  
ic acid amide, 3-amino-4-chloro or 2-chloro-5-  
aminobenzene sulphon-ic acid amide, 2,3-  
dichloro-5-amino- or 2-amino-4,5-dichloro-  
benzene sulphon-ic acid amide, and in addition  
2-trifluoromethyl-4-aminobenzene sulphon-  
ic acid amide and 2-amino-4-trifluoromethyl-5-  
chlorobenzene sulphon-ic acid amide.

As valuable compounds which can be used  
according to the present invention chiefly those  
can be named in which at least one aromatic  
radical is substituted in two positions by halo-  
gen atoms and/or trifluoromethyl groups, this  
substitution advantageously being by halogen  
and trifluoro methyl substituents in the *p*-  
and *m*-positions to the urea bridging member.  
Particularly active are those derivatives in  
which the  $\text{H}_2\text{N}-\text{SO}_2-$  group is in the *m*-  
or preferably in the *o*-position to the  $-\text{NH}-$   
 $\text{CO}-\text{NH}-$  group.

Thus the most valuable compounds corres-  
pond with the general formula:



wherein one U represents  $-\text{SO}_2\text{NH}_2$   
the other U represents hydrogen  
one V represents chlorine or the trifluoro-  
methyl group,  
the other V represents hydrogen or chlorine  
one W represents chlorine or the trifluoro-  
methyl group, and  
the other W represents chlorine.

The activity of such compounds containing  
the  $\text{H}_2\text{N}-\text{SO}_2-$  group could not have been  
foreseen, as if known sulphonated insecticidal  
agents are converted into the corresponding  
 $\text{H}_2\text{N}-\text{SO}_2-$  derivatives by modification of  
their sulphon-ic acid group the insecticidal  
action is reduced to a great extent. Thus for  
example, 2,2<sup>1</sup> - dihydroxy - 3,3<sup>1</sup>,5,5<sup>1</sup> - 4<sup>11</sup> -  
pentachloro - triphenyl methane - 2<sup>11</sup> - sul-  
phon-ic acid amide has not sufficient insecti-  
cidal activity for practical purposes when  
compared with the corresponding sulphon-ic  
acid.

The new compounds according to the present  
invention, however, have remarkable insecti-  
cidal activity and can be used in particular  
for the protection of keratine material against  
injurious pests such as the larvae of moths,  
fur and carpet beetles. In the form of their  
alkali metal salts, e.g. the lithium, sodium and  
potassium salts, they have sufficient water  
solubility to be applied to keratine material  
from such solutions. When applied during the  
dyeing process the compounds draw onto kera-  
tine material, e.g. wool, completely from a  
neutral to weakly acid bath and they are fast  
to washing and rubbing. As has already been  
explained, such insecticidal agents are very

advantageous as they can be used in the same  
dyebath with dyestuffs which draw from a  
neutral to weakly acid medium. However, the  
new compounds can not only be applied in  
aqueous solutions. Those which are soluble in  
organic solvents can also be used in this form  
for the impregnation of keratine material.  
Finally, the compounds can also be used in  
the form of dispersions or in powder form,  
possibly with carriers, as insecticidal agents.

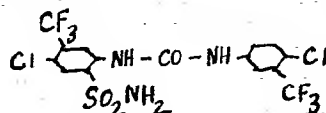
The following examples serve to illustrate  
the invention. Where not otherwise stated, the  
temperatures are in degrees Centigrade and  
the parts are given as parts by weight. The  
relationship of parts by volume to parts by  
weight is as that of litres to kilogrammes.

#### EXAMPLE 1

27.4 Parts of 2- amino - 4 - trifluoro-  
methyl - 5 - chlorobenzene sulphon-ic acid  
amide are dissolved at 50—55° in 250 parts  
of abs. butanone. A solution of 22.1 parts of  
3 - trifluoromethyl - 4 - chlorophenyl iso-  
cyanate in 220 parts of abs. nitrobenzene is  
added and the mixture is heated for 16 hours  
at 40—45° while stirring.

The butanone is then distilled off and, after  
cooling, 200 parts of chlorobenzene are added  
to the residue. The precipitate which forms is  
filtered off, washed with chlorobenzene and  
dried in a vacuum at 100°.

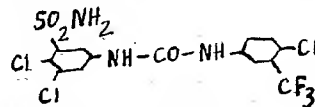
After crystallisation from alcohol, the com-  
pound melts at 208—210°. It corresponds to  
the formula:



Nitrogen determination: found 8.3% N  
calculated 8.4% N

#### EXAMPLE 2

24.1 Parts of 2,3 - dichloro - 5 - amino-  
benzene sulphon-ic acid amide and 22.1 parts  
of 3 - trifluoromethyl - 4 - chlorophenyl iso-  
cyanate are reacted as described in Example  
1. A white body which melts at 235—237°  
is obtained. It corresponds to the formula:

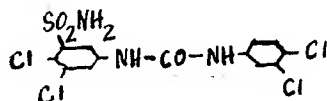


Analysis: found 9.0% N  
calculated 8.9% N

#### EXAMPLE 3

24.1 Parts of 2,3 - dichloro - 5 - amino-  
benzene sulphon-ic acid amide and 18.8 parts  
of 3,4 - dichlorophenyl isocyanate are reacted

as described in the process of Example 1.  
The compound obtained melts at 239—240°  
and corresponds to the formula:



5 Analysis: found 9.8% N  
calculated 9.8% N

## EXAMPLE 4

0.2 Parts of the compound according to Example 2 are dissolved with dilute caustic soda lye and the solution is brought up to 1000 parts by volume with water. 20 Parts of wool are treated in this solution for 30 minutes at 50°.

After rinsing, wringing out and drying, the wool is resistant to attack by the larvae of *Tineola bis.*, *Anthrenus vorax* and *Attagenus piceus*.

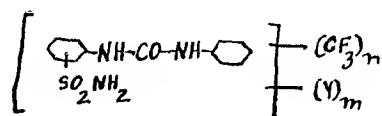
The following compounds can be produced in a manner analogous to those described in the above examples:

No.	M. P.
1	251—252°
2	217—219°
3	260—262°
4	253—255°
5	276—278°
6	280—283°
7	282—285°
8	258—262°
9	218—220°
10	243—245°

No.	M. P.
11	233—235°
12	240—242°
13	224—226°
14	226—228°
15	231—233°
16	238°
17	214°
18	259°
19	239°
20	227°
21	183°
22	210—211°
23	193—195°

## WHAT WE CLAIM IS:—

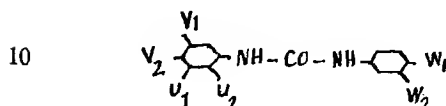
1. A compound having the formula:



wherein

- 5 Y represents halogen,  
n represents an integer from 0 — 2,  
m represents an integer from 0 — 5  
and wherein  $n + m$  are at least 2.

2. A compound having the formula:



wherein one U represents  $-\text{SO}_2\text{NH}_2$ ,  
the other U represents hydrogen,  
one V represents chlorine or the trifluoro-  
methyl group,

- 15 the other V represents hydrogen or chlorine  
and  
one W represents chlorine or the trifluoro-  
methyl group and  
the other W represents chlorine

- 20 3. Process for the production of water  
soluble insecticidal compounds characterised  
by reacting an isocyanate of the aromatic  
series with an aromatic amine, the components  
being so chosen that an  $\text{H}_2\text{N}-\text{SO}_2$  group and

at least two substituents selected from aroma-  
tically bound halogen atoms or trifluoromethyl  
groups are present in the reaction product, the  
 $\text{H}_2\text{N}-\text{SO}_2$  group being introduced with the  
aromatic amine.

4. Manufacture of compounds substantially  
as described with reference to any of the fore-  
going examples 1 to 3.

5 Compounds whenever prepared or pro-  
duced by the processes of manufacture parti-  
cularly described.

6. A compound as specified in any of the  
foregoing examples 1 to 3 or in the Table.

7. Process for the protection of material  
containing keratin fibres characterised by the  
use of any of the compounds as hereinbefore  
claimed by a process substantially as described  
in example 4.

8. Materials containing keratin fibres pro-  
tectively treated with any of the compounds  
defined in claim 1.

9. Manufacture of agents containing insecti-  
cidal compounds for treating keratin fibres  
in an aqueous medium substantially as herein-  
before described.

10. Agents containing insecticidal com-  
pounds for treating keratin fibres in an  
aqueous medium whenever produced as  
claimed in claim 9.

For the Applicants,  
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Reference has been directed, in pursuance  
of Section 8 of the Patents Act, 1949, to  
Specification No. 753,171.